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THERMAL DIFFUSION

- USSR -

by B. A. Geller

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THE CONCENTRATION OF A HEAVY ISOTOPE OF NITROGEN BY THERMAL DIFFUSION

[This is a translation of an article written by B. A. Geller in Zhurnal Fizicheskoy Khimii (Journal of Physical Chemistry), Vol XXX No 8, Moscow, 1956, pages 1,871-1,876.]

We have built an installation for the application of thermal diffusion to gases and we performed a series of experiments for concentrating the N^{15} isotope of nitrogen. These concentrates were used in studies of the mechanism of the condensation of aromatic amines [1]. This article describes the apparatus and the experiments performed, to obtain a 13% N^{15} enriched gas.

Experimental part

The installation (Fig 1) consists of six columns each 3.5 m long and one 1 m in length. The separating columns were of copper and brass and had an inner diameter of 10 mm. Cr-Ni wire, 0.6 mm in diameter, was kept under tension by a spring attached to its lower end, and an alternating current was used to raise its temperature to 800°C. The temperature of the wire which was determined from its expansion, was kept constant by controlling the current. The wire was centered in the column by cross bars of highly annealed pyrophyllite placed at 0.5 m intervals along its length. The connecting tubes between the columns had an inner diameter of only 2-3 mm in order to cut down the extra volume and hence to shorten the time needed to reach equilibrium. In such narrow tubings the thermal convection would have been too small to produce a noticeable separation of the isotopes. Therefore, seven pipe pumps were used. These were placed upon one shaft and rotated by a motor whose speed was reduced to two turns per minute by a reductor. This meant a circulation speed of about 0.4 liter/hour, which was deemed sufficient for equalizing the composition of the gas during its passage from the bottom of one column to the top of the next one.

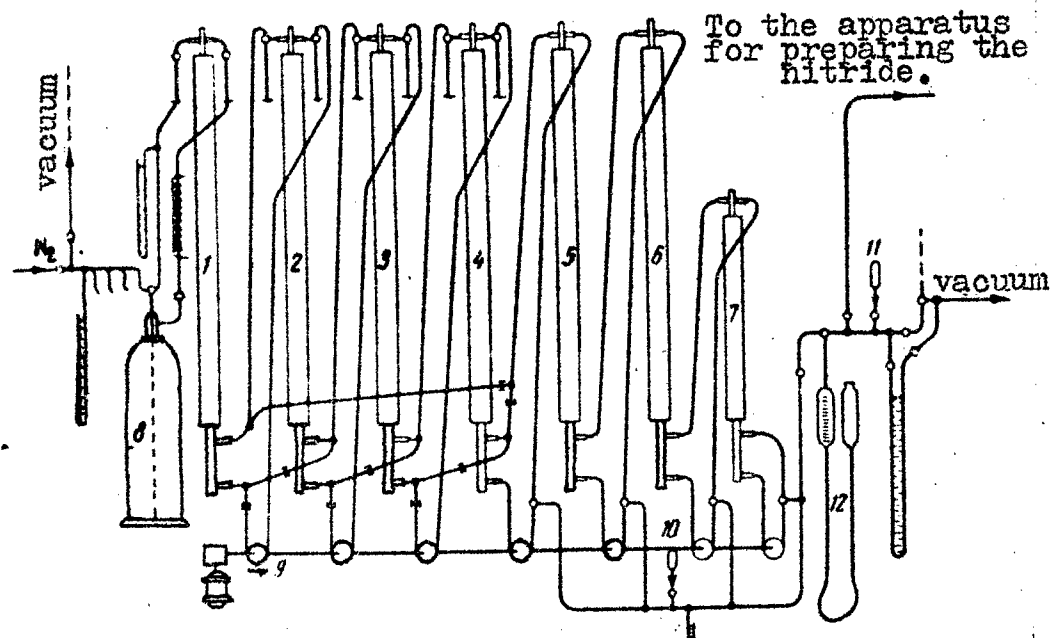


Fig. 1. Diagram of the thermal diffusion installation: 1-7, the columns; 8, one of the four top reservoirs; 9, pumps; 10-11, ampoules for sampling; 12, vessel for the withdrawal of concentrates.

The columns were so connected as to enable them to operate either in cascades or in series. In a cascade scheme equilibrium can be reached in less time, and larger amounts of the heavier isotope can accumulate than would be possible with an arrangement in series. For the cascade process the first four columns were connected in parallel, while each carried a separate, large-volume reservoir on top. The bottom reservoirs were inter-connected and a pump conveyed the gas to the top of the fifth column. The fifth, sixth and seventh columns operated in series. The efficiency of the first five columns was approximately 100 theoretical plates (TT), the sixth had an efficiency of 160 TT, (owing to the presence of perforated disks), the seventh column had an efficiency of 40 TT*. Stopcocks and screw-clamps made it

*The constants of the columns: λ , theoretical length in number of plates and velocity of convection ω , were established by the author in cooperation with S. G. Emidenko in experiments on the separation of mixtures O_2 and N_2 .

possible to connect all columns in series, forming a chain 22 m long with a theoretical efficiency of 730 TT. Three of the upper reservoirs had to be disconnected.

The upper reservoirs were steel tanks of 36-liter capacity. They were connected to the columns by vertical tubings, 17 mm in diameter. The tubings could be heated electrically in order to produce thermal convection.

There was an automatic control insuring stoppage of the current should the supply of cooling water fail. This was done by placing floating contacts at the top of two columns. The contacts actuated a relay fed from storage batteries and were supplied with automatic cutouts.

Samples were obtained through a comb-shaped sampler connected with the last four columns.

Argon-free nitrogen was produced from a mixture of ammonium chloride and sodium nitrite and collected in a gas reservoir of 250-liter capacity. The gas was purified by a sequence of passages through sodium hydroxide, pyrogallol; calcium chloride; soda lime; a furnace with heated copper; calcium chloride, solid KHO , and a trap surrounded with liquid air. Even then the gas still contained about 0.1% of oxygen.

According to A. I. Brodski's [2] theory for an installation with an efficiency of 730 TT (with a separation factor of 1.006 for molecules of N^{14} , N^{15} , and N_2^{14} , calculation has shown that a column working in series and filled with atmospheric nitrogen would reach an equilibrium with 18.5% of N^{15} after 126 days. In a cascade system an equilibrium with 4.1% of N^{15} is reached in five days. Since 17 days were needed to attain this composition in a series system the use of a cascade, preceeding the series system, shortened the time of the operation by 12 days.

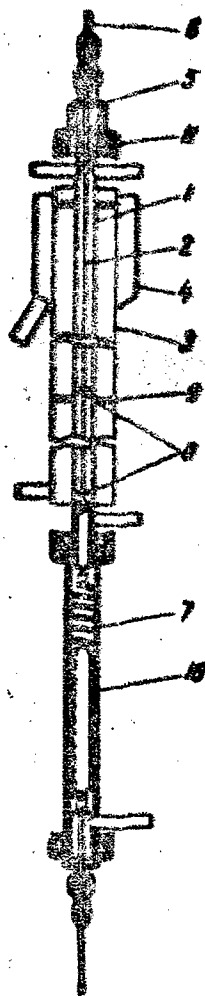


Fig. 2. Diagram of a thermal diffusion column.
 1, separating column; 2, nichrome heating wire; 3, cooler; 4, funnel; 5, hard rubber cap; 6, current inlets, rods; 7, bottom reservoir; 8, wire-centering bars; 9, wire-centering disks; 10, ampoules for volume regulation; 11, shims.

The following is a description of the experiment: The apparatus filled with nitrogen was first put on the cascade system. Six days later, when the concentration of N^{15} reached 4% at the "heavy" end, the columns were switched to the series system, working on one top reservoir placed at the entrance to the apparatus. A pump failure brought the N^{15} concentration down to 1.73% (at the "heavy" end), but the apparatus continued to work in a

series system for 54 days, when the concentration of N^{15} reached 11.5%. At that time samples of the concentrate were taken, and sampling was continued at intervals for 72 days. Samples were taken once a day and collected in a calibrated vessel over liquid mercury. The rate of sampling was varied at different times in order to determine the feasible maximum rate. As a criterion for the correct value of the sample, we used the N^{15} concentration in the gas before and after sampling. The nitrogen in the main reservoir was replaced once by a fresh charge in order that the impoverishment in N^{15} should not affect the enrichment run.

The experiment lasted a total of 213 days. Samples of the enriched gas were transferred into a purifier, where they were freed from oxygen by pyrogallol, dried over sulfuric acid, mixed with pure argon and sent through a tube containing a mixture of $Mg + CaO$ (1:4) chips, heated to 400-500°C. Nitrogen was absorbed quantitatively and turned into nitrides of calcium and magnesium [3].

The contents of the absorber were treated with 60% ethyl alcohol in a still, (in order to forestall explosive action, if treated with water, that might result in a dissociation of the nitrides) and after that with an aqueous solution of $NaOH$. The evolved ammonia was absorbed in a vessel containing chemically pure HCl , the solution was evaporated and the crystallized ammonium chloride subjected to final drying in a desiccator.

The residues of nitrogen left in the apparatus were removed using a mercury burette and treated similarly, thus producing additional amounts of ammonium chloride containing different amounts of N^{15} .

The enrichment run was measured spectroscopically [4]. The test consisted in the examination of the 3,159 Å line of the molecular spectrum of nitrogen. The relative error amounted to 5% for average concentrations (4-10% of N^{15}) and about 10% for lower concentrations [5].

Examination of the results

Efficiency of the cascade process. To compare experimental results with the theory we had to assume a definite value for α , the separation factor. Most of the equations [2, 6-9] offered for the theoretical computation of the thermo-diffusional factor A , which has to be substituted into the equation

$$\alpha = 1 + A \frac{\Delta T}{T_{cp}}, \quad (1)$$

in order to compute α , give for the latter a value much larger than the experimental value. We accepted the Yensen [9] empirical equation

$$A = \frac{1}{6} \frac{\Delta m}{m_{cp}}, \quad (2)$$

which yields A - values that are in fair agreement with experiment. For the separation of the mixture $N_2 + N^{14}N^{15}$ * A becomes 0.0058. With the temperatures of the heated wire at 1,000°K and the cold wall - at 300°K - conditions characteristic of our experiments -- equation (1) yields the value of 1.006 for α , which agreed well with our value of 1.0057 obtained in earlier experiments at an equilibrium concentration of 6% $N^{14}N^{15}$ in a cascade system equivalent to about 370 Tl. Thus, from Raleigh's equation

$$\frac{N}{1-N} \frac{1-N_0}{N_0} = \alpha^p, \quad (3)$$

where $p = 410$, $N_0 = 0.0076$ and $\alpha = 1.006$ we obtain for our cascade system a maximum concentration of 8.2% of $N^{14}N^{15}$ or 4.1% for N^{15} . An experiment lasting six days resulted in a concentration of 3.7% of N^{15} .

The time required for reaching equilibrium has been calculated by the equation of A. I. Brodski' [2]. In our cascade complete uniformity of transfer of N^{15} in all sections was not attained, and the required time for equilibrium was calculated as follows: each section of the cascade was considered as a separate column, the whole balance of the "heavy" part being assumed to act as the bottom reservoir. Since the volumes of all parts were known and the concentrations of N^{15} in them could be determined, it was simple to calculate the volume of the gas in the bottom reservoir that it would have occupied at the concentration of the N^{15} in the lower reservoir -7- of the column under consideration. For example, should the concentration of N^{15} in the bottom of the column be

*Dissociation of the molecules of nitrogen along the heated wire proceeds very slowly, therefore, normally only the molecules $N^{14}N^{15}$ are subject to enrichment. Atmospheric nitrogen contains no more than 0.0014% of N^{15} and this amount cannot produce any noticeable effect.

2%, while the bottom reservoir of volume V be filled with gas containing 4% N^{15} , the reduced volume of that reservoir would be $V \cdot \frac{1}{2} = 2V$. Summing up the thus-computed volumes of the lower reservoirs we would obtain the reduced volume of a gas containing 2% N^{15} .

By using the actual and the reduced volumes and the concentrations of N^{15} at the top and bottom of each section, we can easily compute the time needed for reaching equilibrium from the following equation for the steady state of a simple column:

$$t_p = \frac{VK}{w} (N - N_0) + \frac{HK}{wP \lg \alpha} \left(\lg \frac{1 - N_0}{1 - N} - N_0 P \lg \alpha \right). \quad (4)$$

In this equation N_0 is the original concentration of N^{15} ; N , the final molar concentrations of N^{15} ; t , the duration of the experiment in hours; t_p , time of equilibrium; P , the theoretical number of plates; λ , the length of a theoretical plate in cm; V , the volume of the lower reservoir in ml; H , the volume of the working column in ml; w , the rate of convection in ml/hr;

$K = \frac{1 - N_0 \beta}{N_0 (1 - N_0 \beta)}$, where $\beta = \frac{\alpha - 1}{\alpha}$; n , the transfer of the heavy isotope in ml/hr; g , the efficiency of the column ml/hr.

The results of the computations with the original lengths of three sections of 3.5 m and the end 1-m tube, $\lambda = 3.3, 3.3, 2.2, 2.4$ cm $P = 105, 105, 160$ and 40, $w = 5,080, 1,270, 1,150, 265$ ml/hr for each section and the end tubing are given in the table.

Section	Calculated magnitudes							
	N_0 molar fraction	N molar fraction	K	n ml/hr	g ml/hr	H ml	v_{np} ml	t_p hours
I	0.0076	0.0142	22230	0.230	16.1	1096	2175	80
II	0.0142	0.0265	11945	0.106	4.0	274	904	118
III	0.0265	0.0659	6492	0.177	2.7	274	139	57
Final Tubing	0.0659	0.0825	2722	0.097	1.2	78	14	9

The total time needed for the attainment of equilibrium throughout the whole apparatus appears to be determined by the maximum value given in the table, or about five days. This figure is in satisfactory agreement with the experimental value of six days, during which the

concentration almost reached the equilibrium value.

Kinetics of concentration. Curve 1, Fig 3, shows the variation of the concentration for the combined system, i. e., the cascade process (lower part of the graph) preceded and was switched over to the series (upper part of the graph). Experimental points coincide satisfactorily with the theoretical curve. The series portion of curve 1 and the total length of curve 2, corresponding strictly to a series process, were calculated from equation (5), which relates the concentration and the time needed for reaching equilibrium*.

$$t = \frac{VK}{w}(N - N_0) + \frac{HK}{w\rho \lg a} \left(\lg \frac{1-N_0}{1-N} - N_0 \lg \frac{N}{1-N} \frac{1-N_0}{N_0} \right) \quad (5)$$

In curve 2 the coordinates of time must be considered as representative, since upon the failure of the pump the experimental points were plotted against the original conditions with $N_0 = 1.73\%$ and $t =$ seven days (the time obtained by placing the value of 1.73% on the theoretical curve). Other points fitted that graph quite well.

Satisfactory agreement was obtained between experiment and theory for the kinetics of H^{15} concentration at two time intervals of sampling: 111 and 151 days. The latter results are shown in Fig 3 by two little triangles, which correspond to the upper coordinate of time. The curve passing through these two points coincides with the theoretical curve 2.

This satisfactory agreement between theory and experiment indicates that the break during the process had little effect on the results.

*The calculation was made using the following values:

$V = 15$ ml, $H = 1,722$ ml, $w = 1,270$ ml/hr, $a = 1.006$,
 $N_0 = 0.0076$, $\rho = 730$.

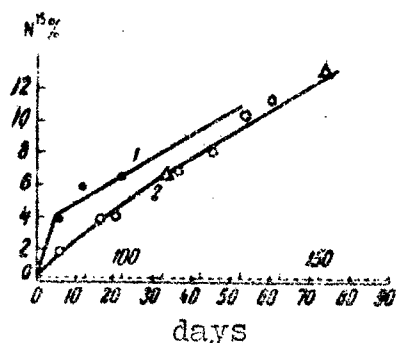


Fig 3

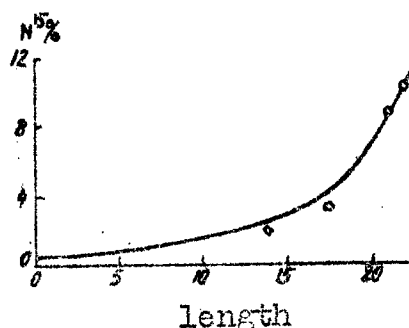


Fig 4

Fig 3 Kinetics of the concentration process. Curve 1 combination process, curve 2 serial process.

Fig 4 Distribution of N^{15} concentration along the length of the column.

Productivity of the apparatus. Calculation [27] shows that the transfer of pure N^{15} would equal 0.028 ml/hr. This would correspond to 0.28 ml/hr for a gas containing 10% of N^{15} . In practice the yield was somewhat lower - the process slowed down considerably when a yield of 0.24 ml/hr, (a N^{15} concentration of 9%) had been reached. When 0.17 ml of gas were withdrawn per hour (at a concentration of 10.5% N^{15}) the concentration at the "heavy" end was still rising. Thus it may be assumed that the proper withdrawal amounted to 0.2 ml per hour at a N^{15} concentration of 10%.

Distribution of N^{15} along the length of the apparatus. This is shown in Fig 4. It is calculated on the basis of the maximum concentration of N^{15} reached on the 74th day of operation. Points obtained from the analyses of the concentrated gas from the fourth, fifth, and sixth columns satisfactorily conform to the theoretical curve.

In conclusion, we shall compare the efficiency of our apparatus with the installations described in the literature. Recently Davenport and Winter [10] used a column 316 cm long and found an equilibrium concentration 1.59 times the original one at a pressure of 0.5 atm. Our columns, working far below equilibrium, yielded a concentration factor of 1.17 per meter, or a total of 1.65 if our columns also had been 316 cm long.

The columns of Clausius [6], who started with N^{15} concentration between 5 and 8% and obtained pure N^{15} , had

a characteristic length of 410 cm ($d = 12\text{ mm}$ with 15 plates for 285 cm of length), and 239 cm ($d = 9.2 - 8.6\text{ mm}$, with plates for 285 cm). Our columns had a theoretical length of 510 cm ($d = 10\text{ mm}$ without plates) and 340 cm ($d = 10\text{ mm}$ with six plates). This comparison corroborates the positive effect of the plates upon the separation of the isotopes.

I am grateful to A. I. Brodski' for suggesting the theme and for his advice during the investigation.

Conclusions

1. The investigations covered the concentration of heavy nitrogen by thermal diffusion in a system of seven columns having a total length of 22 m , with a theoretical efficiency of 730 plates (TT). The experiment lasted 213 days. The maximum concentration reached was 12.9% of N^{15} .

2. The kinetics of the process has been examined along the length of the apparatus. The results coincided fairly well with Brodski's theory. Maximum efficiency was found to be 0.20 ml/hr at 10% of N^{15} .

3. Pure ammonium chloride (6.1 g) containing from 1.2 to 9.0% of N^{15} was produced, which is suitable for isotopic investigations.

Academy of Sciences UkrSSR
Institute of Physical Chemistry
imeni L. V. Pisarzhevskiy
Kiev

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*This is the length of column corresponding to an enrichment of e (2.718) times.

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